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(54) Title: PERFUMED BLEACHING COMPOSITIONS

(57) Abstract

There is provided a perfumed bleaching composition containing: (a) a hydrophobic bleaching system selected from (i) a perhydrate in amount of from 0.1 % to 60 % by weight and combined with a hydrophobic peroxyacid bleach precursor in amount of from 0.1 % to 60 % by weight, (ii) a preformed hydrophobic peroxyacid in amount of from 0.1 % to 60 % by weight, and (iii) mixtures of (i) and (ii), wherein a hydrophobic peroxyacid bleach precursor is defined as a compound which produce under perhydrolysis a hydrophobic peroxyacid whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre, and wherein a hydrophobic preformed peroxyacid is defined as a compound whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre, and (b) a perfume composition in amount from 0.05 % to 2 % by weight which comprises one or more aroma chemicals selected from: tertiary alcohols, nitriles, lactones, ketones, acetals, ethers, schiff bases, esters and mixtures thereof, wherein the total sum of the weight of said aroma chemicals in the perfume is at least 40 % by weight of the perfume.

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PERFUMED BLEACHING COMPOSITIONS

Field of the invention

The invention relates to perfumed bleaching compositions. More specifically, it relates to bleaching compositions comprising a hydrophobic bleach system and a stabilised perfume composition.

Background of the invention

Perfumes are an important and desirable part of detergent compositions. They are used to cover up the chemical odours of the cleaning ingredients and provide an aesthetic benefit to the wash process and, preferably the cleaned fabrics. EP 430315, which discloses the use of a laundry detergent composition containing a lipase and a perfume having specific fragrance materials, exemplifies such use. In said patent, the perfume composition is said to counteract the problem of the residual malodour of lipase treated laundry.

A problem encountered with perfumes is their volatility and many perfume ingredients can be destroyed or damaged in presence of cleaning ingredients, especially alkali and bleaches.

Hydrophobic bleach systems selected from a source of hydrogen peroxide combined with a hydrophobic peroxyacid bleach precursor and a hydrophobic peroxyacid bleach are known in the art as effective soil removal agents of dingy stains.

The Applicants have found that the problem of perfume oxidation may be particularly troublesome with hydrophobic peroxyacid bleach precursors which on perhydrolysis produce a peroxyacid which is an

amido substituted peroxyacid. Precursor compounds as well as peroxyacid compounds per se of the amido substituted type, in particular, have also been found to give rise to the problem.

One solution to this problem is encapsulation of the perfume. This increases the expense and complexity of the formulation and does not always provide sufficient protection. EP 332259 teaches the use of a liquid detergent composition containing peroxyacid bleach and perfumed silica particles which protect the perfume from oxidation by the bleach.

Another solution to this problem is the reduction in the level of the hydrophobic bleach system. Whilst reducing the level of the hydrophobic bleach system employed in the wash tends to ameliorate these problems, this is accompanied by a marked negative effect on the dingy stains/soil removal ability.

The detergent formulator thus faces the challenge of formulating a product which maximises soil/stain removal, which avoids degradation of the detergent components, which covers up the chemical odours of the cleaning ingredients, which provides an aesthetic benefit and which is also inexpensive.

The Applicants have now surprisingly found that the provision of a minimum amount of specific perfume raw materials allows the use of stabilised perfumed compositions in presence of a hydrophobic bleach system.

The Applicants have also surprisingly found, that delivery of the perfume on the fabric is enhanced with hydrophobic peroxyacid precursor. Not to be bound by theory, it is believed that the hydrophobic peroxyacid precursor serves as a carrier material for the perfume composition.

It is therefore an object of the present invention to provide compositions suitable for use in laundry washing methods which produces an excellent perfume fragrance on fabrics as well as an

excellent perfume stability in presence of the hydrophobic bleaching system in the wash liquor and in the product during storage.

It is a further object of the invention to provide compositions suitable for use in laundry washing methods which produce effective dingy soil removal.

Summary of the invention

The present invention relates to a perfumed bleaching composition containing:

a-a hydrophobic bleaching system selected from

- i)-a perhydrate in amount of from 0.1% to 60% by weight and combined with a hydrophobic peroxyacid bleach precursor in amount of from 0.1% to 60% by weight,
- ii)-a hydrophobic preformed peroxyacid in amount of from 0.1% to 60% by weight, and
- iii)-mixtures of i) and ii),

wherein a hydrophobic peroxyacid bleach precursor is defined as a compound which produces under perhydrolysis a hydrophobic peroxyacid whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre, and wherein a hydrophobic preformed peroxyacid is defined as a compound whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre, and

b- a perfume composition in amount from 0.05% to 2% by weight which comprises one or more aroma chemicals selected from: tertiary alcohols, nitriles, lactones, ketones, acetals, ethers, schiff bases, esters and mixtures thereof, wherein the total sum of the weight of said aroma chemicals in the perfume is at least 40% by weight of the perfume.

Detailed description of the invention

An essential component of the invention is a hydrophobic bleach system selected from a perhydrate combined with a hydrophobic

peroxyacid bleach precursor, a preformed hydrophobic peroxyacid and any mixtures thereof.

Perhydrate bleach

The perhydrate is typically an inorganic perhydrate bleach, normally in the form of the sodium salt, as the source of alkaline hydrogen peroxide in the wash liquor. This perhydrate is normally incorporated at a level of from 0.1% to 60%, preferably from 3% to 40% by weight, more preferably from 5% to 35% by weight and most preferably from 8% to 30% by weight of the composition.

The perhydrate may be any of the alkali metal inorganic salts such as perborate monohydrate or tetrahydrate, percarbonate, perphosphate and persilicate salts but is conventionally an alkali metal perborate or percarbonate.

Sodium percarbonate, which is the preferred perhydrate, is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. Most commercially available material includes a low level of a heavy metal sequestrant such as EDTA, 1-hydroxyethylidene 1, 1-diphosphonic acid (HEDP) or an amino-phosphonate, that is incorporated during the manufacturing process. For the purposes of the detergent composition aspect of the present invention, the percarbonate can be incorporated into detergent compositions without additional protection, but preferred executions of such compositions utilise a coated form of the material. A variety of coatings can be used including borate, boric acid and citrate or sodium silicate of $\text{SiO}_2:\text{Na}_2\text{O}$ ratio from 1.6:1 to 3.4:1, preferably 2.8:1, applied as an aqueous solution to give a level of from 2% to 10%, (normally from 3% to 5%) of silicate solids by weight of the percarbonate. However the most preferred coating is a mixture of sodium carbonate and sulphate or sodium chloride.

The particle size range of the crystalline percarbonate is from 350 micrometers to 1500 micrometers with a mean of approximately 500-1000 micrometers.

Hydrophobic peroxyacid bleach precursor

One form of the essential hydrophobic bleach system component of the invention is a hydrophobic peroxyacid bleach precursor which produces upon perhydrolysis hydrophobic peroxyacid whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre and wherein said critical micelle concentration is measured in aqueous solution at 25°C.

Preferably, the peroxyacid backbone chain contains at least 7 carbons which may be linear or partly or totally branched or cyclic and any mixtures thereof.

The peroxyacid bleach precursors are normally incorporated at a level of from 0.1% to 60%, preferably from 3% to 40% and most preferably 3 to 25% by weight of the perfumed bleaching composition.

Preferably, hydrophobic peroxyacid bleach precursor compounds are selected from bleach precursor compounds which comprise at least one acyl group forming the peroxyacid moiety bonded to a leaving group through an -O- or N- linkage.

Suitable peroxyacid bleach precursors for the purpose of the invention are the amide substituted compounds of the following general formulae:

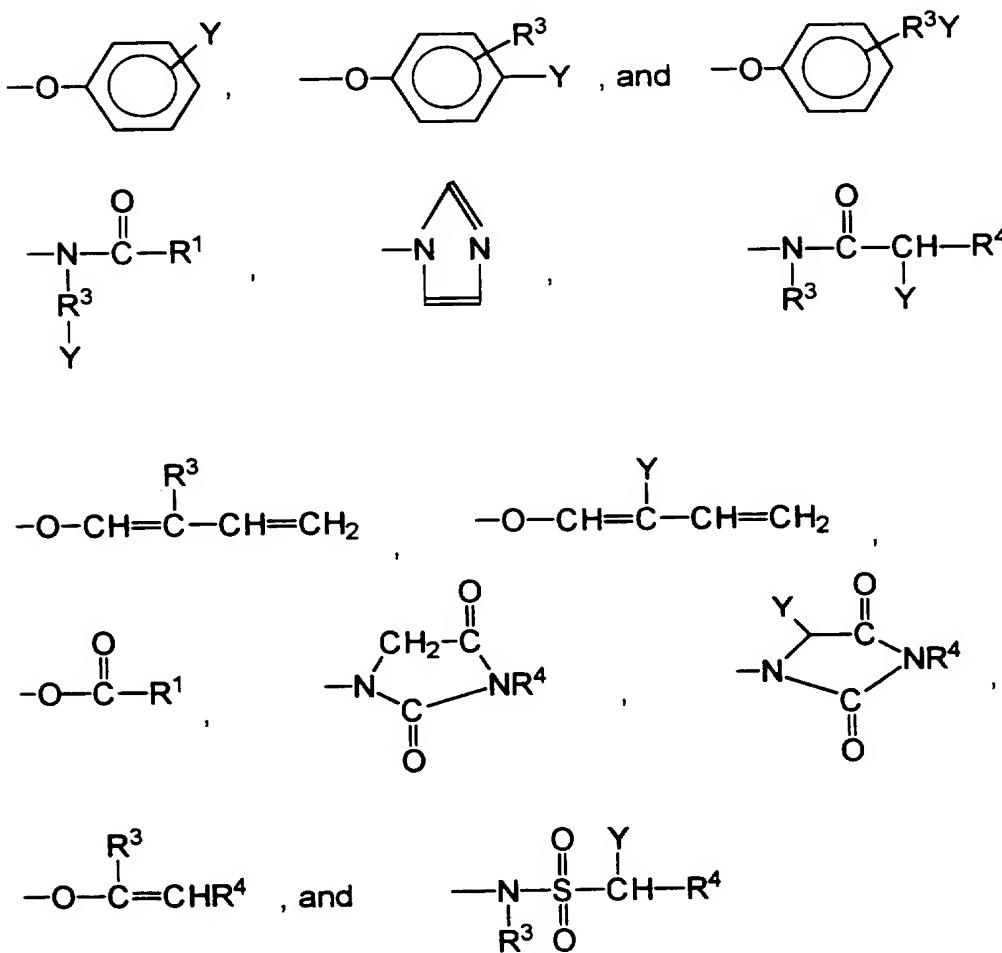


wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from about 6 to 12 carbon atoms. R^2 preferably contains from about 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be

sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2 . R^2 can include alkyl, aryl, wherein said R^2 may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from:



and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group. Any of R^1 , R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups

The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and $O<--N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Other suitable L group for use herein, include a leaving group selected from a caprolactam leaving group, a valerolactam leaving group and mixture thereof.

Preferred examples of bleach precursors of the above formulae include amide substituted peroxyacid precursor compounds selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-nanonamidocaproyl)oxy benzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in EP-A-0170386.

Still another class of bleach precursor is the class of alkyl percarboxylic acid bleach precursors. Preferred alkyl percarboxylic acid precursors include nonanoyl oxy benzene sulphonate (NOBS described in US 4,412,934) and 3,5,5-tri-methyl hexanoyl oxybenzene sulfonate (ISONOBS described in EP120,591) and salts thereof.

Mixtures of any of the peroxyacid bleach precursor, herein before described, may also be used.

In addition, conventional peroxyacid bleach precursors such as the tetraacetyl ethylene diamine (TAED) bleach precursor may be added to the bleaching composition of the invention so as to produce an enhanced soil removal performance.

Preformed hydrophobic peroxyacid compound

Another form of the essential hydrophobic bleach system component of the invention is a preformed hydrophobic peroxyacid bleaching agent and salt thereof whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre and wherein said critical micelle concentration is measured in aqueous solution at 25°C.

Preferably, the peroxyacid backbone chain contains at least 7 carbons which may be linear, partly or totally branched, or cyclic and any mixtures thereof.

Preferably, hydrophobic peroxyacid bleach compounds are selected from peroxyacid bleach compounds which comprise at least one acyl group forming the peroxyacid moiety bonded to a leaving group through an -O- or -N- linkage.

Preformed hydrophobic peroxyacid compounds will typically be in amount of from 0.1% to 60%, preferably from 3% to 20% by weight.

Suitable examples of this class of agents include (6-octylamino)-6-oxo-caproic acid, (6-nonylamino)-6-oxo-caproic acid, (6-decylamino)-6-oxo-caproic acid, magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent 4,634,551, EP 0,133,354, U.S. Patent 4,412,934 and EP 0,170,386. A preferred hydrophobic preformed peroxyacid bleach compound for the purpose of the invention is monononylamido peroxycarboxylic acid.

Perfume composition

The other essential component of the invention is a perfume composition comprising one or more aroma chemicals selected from

tertiary alcohols, nitriles, lactones, ketones, acetals, ethers, schiff bases, esters and mixtures thereof.

The perfume composition is incorporated in the bleaching composition of the invention at a level of from 0.05% to 2% by weight, preferably from 0.01% to 1% by weight of the bleaching composition.

The total sum of the weight of said aroma chemicals present in the perfume composition is at least 40%, preferably at least 50% and more preferably at least 60% by weight of the perfume.

For the purpose of the invention, aroma chemicals selected from tertiary alcohols, nitriles, lactones, ketones, acetals, ethers and schiffs bases can be either saturated or unsaturated. When in unsaturated form, they comprise a group selected from an aromatic ring and an alkenyl group and mixtures thereof.

For the purpose of the invention, aroma chemicals of the ester class can be saturated or unsaturated. When in unsaturated form, they either comprise an alkenyl group or are esters of salicylic acid.

Non-limiting tertiary alcohols suitable for the purpose of the invention include tetrahydro linalool, tetrahydro myrcenol, tetrahydro muguol and tetrahydro geraniol compounds and mixtures thereof.

When used such tertiary alcohol compounds will be at a level of up to 50%, preferably at a level of up to 30% and more preferably up to 20% by weight of the perfume composition.

Non-limiting examples of nitriles suitable for the purpose of the invention include lauric nitrile, myristic nitrile and tridecene-2-nitrile compounds, and mixtures thereof.

When used such nitrile compounds will be at a level of up to 10%, preferably at a level of up to 5% by weight of the perfume composition.

Non-limiting examples of lactones suitable for the purpose of the invention include undecalactone, hexadecanolide and cyclopentadecanolide compounds.

When used such lactones will be at a level of up to 30%, preferably at a level of up to 20% by weight of the perfume composition.

Non-limiting examples of ketones suitable for the purpose of the invention include methyl beta naphtyl ketone, methyl phenyl ethyl ketone and 7-acetyl 1,2,3,4,5,6,7,8 octanhydro 1,1,6,7 tetra methyl naphtalene compounds.

When used such ketones will be at a level of from up to 40%, preferably at a level of up to 30% and more preferably up to 20% by weight of the perfume composition.

Non-limiting examples of acetals suitable for the purpose of the invention include (indan-alpha-ole, 2-hydroxymethylene) formald acetal, acetaldehyde: phenyl ethyl propyl acetal and 4-phenyl-2,4,6-trimethyl-1-3-dioxane compounds.

When used such acetals will be at a level of up to 20%, preferably at a level of up to 10% by weight of the perfume composition.

Non-limiting examples of ethers suitable for the purpose of the invention include iso-amyl phenyl ethyl ether, phenyl ethyl methyl ether, cedryl methyl ether and 3,3,5 trimethyl cyclohexyl ethyl ether compounds.

When used such ethers will be at a level of up to 20%, preferably at a level of up to 10% by weight of the perfume composition.

Non-limiting examples of schiffs bases suitable for the purpose of the invention include lyral/methyl anthranilate, helional/methyl anthranilate and triplal/methyl anthranilate.

When used such schiffs bases will be at a level of up to 15%, preferably at a level of up to 10% and more preferably up to 5% by weight of the perfume composition.

Non-limiting examples of esters suitable for the purpose of the invention include 2-tertiary butyl cyclohexyl acetate, 4-tertiary butyl cyclohexyl acetate, hexahydro 4-7-methano-inden-5-yl acetate, hexahydro 4-7-methano-inden-6-yl acetate, hexahydro 4-7-methano-inden-5-yl propionate, hexahydro 4-7-methano-inden-6-yl propionate, hexyl salicylate and amyl salicylate compounds.

When used such esters will be at a level of up to 60%, preferably at a level of up to 40% and more preferably up to 30% by weight of the perfume composition.

For the purposes of the present invention, a perfumed bleaching composition consists of a bleaching composition and a perfume composition, wherein said perfume is incorporated by any means in a composition selected from:

- i)-the bleaching composition as a finished product,
- ii)-the bleaching composition during its making process, or any mixtures thereof.

For the purposes of the invention, a detergent composition incorporating a perfumed bleaching composition consists of a bleaching composition, a perfume composition, one or more surfactants, one or more builders and optionally other conventional detergent ingredients, wherein said perfume is incorporated by any means in a composition selected from:

- iii) a detergent composition, as a finished product, and incorporating a bleaching composition,
- iv) a detergent composition, during its making process, and incorporating a bleaching composition,

- v) a bleaching composition as defined hereinbefore in i) and/or ii) and further incorporated in a detergent composition and any mixtures thereof.

Processes for incorporating the perfume in the bleaching composition are not critical to the present invention. This can be done by spray-on, admixture with one or more components of the bleaching composition or other means known to the man skilled in the art. A preferred process, for cost and practicability reasons, is a spray-on process.

The bleaching composition of the invention may also contain additional components which are not detrimental to the perfume composition. Such additional compounds may include fillers such as sodium sulphate.

The detergent composition aspect of the invention comprises the incorporation of the herein before described perfumed bleaching composition together with a surfactant material, a builder, and optionally other components conventional in detergent compositions.

Detergent compositions incorporating the perfumed bleaching composition will normally contain from 0.1% to 60% of said perfumed bleaching composition, more frequently from 2% to 40% and most preferably from 5% to 30%, on a composition weight basis.

Such detergent compositions will contain a surfactant material, a builder and preferably will also contain other components conventional in detergent compositions. Thus, preferred detergent compositions will incorporate one or more surfactants, builders together with one or more soil suspending and anti-redeposition agents, suds suppressors, enzymes, fluorescent whitening agents, photoactivated bleaches and colours.

Surfactants

Detergent compositions incorporating the perfumed bleaching composition of the invention of the present invention will include one or more surfactants.

The total amount of surfactants will be generally up to 70%, typically 1 to 55%, preferably 1 to 30%, more preferably 5 to 25% and especially 10 to 20% by weight of the total composition.

Nonlimiting examples of surfactants useful herein include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺)CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺)CH₂CH₃ where x and (y + 1) are integers of at least 7, preferably at least 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AExS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-C₁₈ glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE"), including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used.

Other suitable surfactants suitable for the purpose of the invention are the anionic alkali metal sarcosinates of formula:



wherein R is a C₉-C₁₇ linear or branched alkyl or alkenyl group, R₁ is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the lauroyl, cocoyl (C₁₂-C₁₄), myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

Still another class of surfactant which may be suitable for the purpose of the invention are the cationic surfactant. Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Builders - Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. Granular formulations typically comprise from 10% to 80%, more typically from 15% to 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or phosphate-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates).

Non-phosphate builders may also be used. These can include, but are not restricted to phytic acid, silicates, alkali metal carbonates (including bicarbonates and sesquicarbonates), sulphates, aluminosilicates, monomeric polycarboxylates, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, organic phosphonates and aminoalkylene poly (alkylene phosphonates).

The compositions herein also function in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the so called 'amorphous' alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and crystalline layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminium. NaSKS-6 has the delta- $\text{Na}_2\text{Si}_2\text{O}_5$ morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- $\text{Na}_2\text{Si}_2\text{O}_5$ (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilising agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973. Such carbonate builders act as builders to remove divalent metal ions such as calcium and additionally provides alkalinity and aids in soil removal.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to 0.5, and x is an integer from 15 to 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or

synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from 20 to 30, especially 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralised salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in U.S. Patent 3,128,287 and U.S. Patent 3,635,830. See also "TMS/TDS" builders of U.S. Patent 4,663,071. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, or acrylic acid, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-

tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the compositions containing the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in EP 0,200,263.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226 and in U.S. Patent 3,308,067. See also U.S. Pat. 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Conventional detergent ingredients

Chelants

Chelating agents generally comprise from 0.1% to 10% by weight of the compositions herein. More preferably, if utilized, the chelating agents will comprise from 0.1% to 3.0% by weight of such compositions.

A chelating agent can be selected from amino carboxylate, organic phosphonate, polyfunctionally-substituted aromatic compound, nitriloacetic acid and mixture thereof. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove transition metal ions such as iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, ethylenediamine disuccinate, N-hydroxyethylenediaminetriacetates, 2-hydroxypropylene diamine disuccinate, nitrilotriacetates, ethylenediamine tetrapropionate, triethylenetetraaminehexacetates, ethylene triamine pentaacetate, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Preferred amino carboxylates chelants for use herein are ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, ethylenediamine-N,N'-diglutamate (EDDG) and 2-hydroxypropylene-diamine-N,N'-disuccinate (HPDDS) compounds.

A most preferred amino carboxylate chelant is ethylenediamine disuccinate.

Organic phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylene phosphonates) available under the trademark DEQUEST from Monsanto, diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene

phosphonate), hexamethylene diamine tetra (methylene phosphonate), α -hydroxy-2 phenyl ethyl diphosphonate, methylene diphosphonate, hydroxy 1,1-hexylidene, vinylidene 1,1 diphosphonate, 1,2 dihydroxyethane 1,1 diphosphonate and hydroxy-ethane 1,1 diphosphonate.

Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than 6 carbon atoms.

Preferred chelants are the diphosphonate derivatives selected from α -hydroxy-2 phenyl ethyl diphosphonate, methylene diphosphonate, hydroxy 1,1-hexylidene, vinylidene 1,1 diphosphonate, 1,2 dihydroxyethane 1,1 diphosphonate and hydroxy-ethane 1,1 diphosphonate. A most preferred is hydroxy-ethane 1,1 diphosphonate.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

Enzymes - Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of fugitive dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability and stability versus active detergents and builders. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5% by weight of a commercial enzyme preparation.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see EP 130,756) and Protease B (see EP257189). Preferred levels of proteases are from 0.01% to 4.0% by weight of the detergent composition herein.

Amylases include, for example, α -amylases described in GB 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries. Fungamyl (Novo) is especially useful. Preferred levels of amylases are from 0.01% to 2.0% by weight of the detergent composition herein.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. ENDO A, CAREZYME both from Novo Industries A/S are especially useful. Preferred levels of cellulases are from 0.01% to 1.0% by weight of the detergent composition herein.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name

Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases *ex* Chromobacter viscosum, e.g. Chromobacter viscosum var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases *ex* Pseudomonas *gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EP 341,947) is a preferred lipase for use herein. Preferred levels of lipases are from 0.01% to 2.0% by weight of the detergent composition herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139. Enzymes are further disclosed in U.S. Patent 4,101,457 and in U.S. Patent 4,507,219. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. Patent 3,600,319 and EP 0 199 405. Enzyme stabilisation systems are also described, for example, in U.S. Patent 3,519,570.

Enzyme Stabilisers - The enzymes employed herein are stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of

cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilisers, especially borate species: see Severson, U.S. 4,537,706. Typical detergents, especially liquids, will comprise from 1 to 30, preferably from 2 to 20, more preferably from 5 to 15, and most preferably from 8 to 12, millimoles of calcium ion per litre of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from 0.05 to 0.4 millimoles per litre, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from 0.05% to 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from 0.25% to 10%, preferably from 0.5% to 5%, more preferably from 0.75% to 3%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the

basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from 0.5% to 8%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from 2,000 to 10,000, more preferably from 4,000 to 7,000 and most preferably from 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this

type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from 2,000 to 100,000, more preferably from 5,000 to 75,000, most preferably from 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from 30:1 to 1:1, more preferably from 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from 500 to 100,000, preferably from 1,000 to 50,000, more preferably from 1,500 to 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of 10,000.

Clay Soil Removal/Anti-redeposition Agents - The compositions according to the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from 0.01% to 10.0% by weight of

the water-soluble ethoxylates amines; liquid detergent compositions typically contain 0.01% to 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in EP 111,965. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in EP 111,984; the zwitterionic polymers disclosed in EP 112,592; and the amine oxides disclosed in U.S. Patent 4,548,744. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Soil Release Agent - Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterised by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

Soil release agents characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones (see EP 0 219 048). Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release

agent is in the range of from 25,000 to 55,000. See U.S. Patent 3,959,230 to Hays and U.S. Patent 3,893,929.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units which contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Patent 4,968,451. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580 and the block polyester oligomeric compounds of U.S. Patent 4,702,857.

Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

If utilized, soil release agents will generally comprise from 0.01% to 10.0%, by weight, of the compositions herein, typically from 0.1% to 5%, preferably from 0.2% to 3.0%.

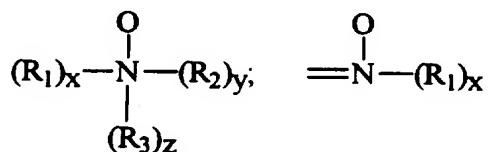
Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from 1.7 to 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from 0.5% to 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

Dye Transfer Inhibiting Agents

The compositions according to the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from 0.01% to 10% by weight of the composition, preferably from 0.01% to 5%, and more preferably from 0.05% to 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: $-NC(O)-$, $-C(O)O-$, $-S-$, $-O-$, $-N=$; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $pK_a < 10$, preferably $pK_a < 7$, more preferred $pK_a < 6$.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls,

polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful in the compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of 50,000 and an amine to amine N-oxide ratio of 1:4.

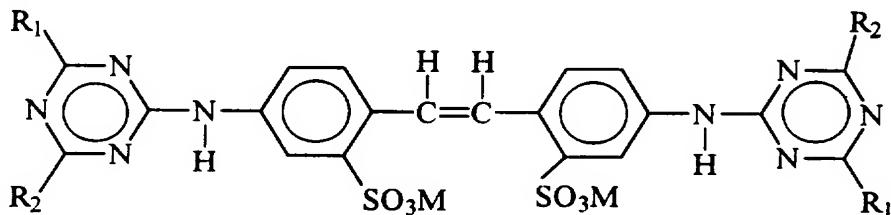
Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization".) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from 5,000 to 400,000, preferably from 5,000 to 200,000, and more preferably from 5,000 to 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from 500 to 100,000, preferably from 1,000 to 10,000. Preferably, the ratio of

PEG to PVP on a ppm basis delivered in wash solutions is from 2:1 to 50:1, and more preferably from 3:1 to 10:1.

The detergent compositions herein may also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from 0.01% to 1.2% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Other specific optical brightener species which may be used in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Conventional optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from 0.005% to 5%, preferably from 0.01% to 1.2% and most preferably from 0.05% to 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John

Wiley & Sons, New York (1982). Further optical brightener which may also be used in the present invention include naphthalimide, benzoxazole, benzofuran, benzimidazole and any mixtures thereof.

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD; the 2-(4-styryl-phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-benzimidazol-2-yl)ethylene; 1,3-diphenyl-pyrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphtho-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho[1,2-d]triazole. See also U.S. Patent 3,646,015.

Suds Suppressors - Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols,

aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of -40°C and 50°C, and a minimum boiling point not less than 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from 12 to 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779 and EP 354016.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672 and in U.S. Patent 4,652,392.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from 20 cs. to 1,500 cs. at 25°C;
- (ii) from 5 to 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(CH_3)_3SiO_{1/2}$ units of SiO_2 units in a ratio of from $(CH_3)_3SiO_{1/2}$ units and to SiO_2 units of from 0.6:1 to 1.2:1; and
- (iii) from 1 to 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from 0.001 to 1, preferably from 0.01 to 0.7, most preferably from 0.05 to 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471 and 4,983,316; 5,288,431 and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than 1,000, preferably between 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a

solubility in water at room temperature of more than 2 weight %, preferably more than 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than 1,000, more preferably between 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to 5%, by weight, of the detergent composition. Preferably, from 0.5% to 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized

in amounts up to 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from 0.01% to 1% of silicone suds suppressor is used, more preferably from 0.25% to 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from 0.1% to 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from 0.01% to 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, as well as other softener clays known in the art, can optionally be used typically at levels of from 0.5% to 10%, preferably from 0.5% to 2% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416 and U.S. Patent 4,291,071.

Other Ingredients - A wide variety of other functional ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl₂, MgSO₄, and the like, can be added at levels of, typically,

0.1%-2%, to provide additional suds and to enhance grease removal performance.

Various detergents ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the detergents ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detergents ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended detergents function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C₁₃-15 ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between 6.5 and 11, preferably between 7.5 and 10.5. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

Form of the compositions

The detergent compositions of the invention can be formulated in any desirable form such as powders, granulates, pastes, liquids, and gels.

Liquid compositions

The detergent compositions of the present invention may be formulated as liquid detergent compositions. Such liquid detergent compositions typically comprise from 94% to 35% by weight, preferably from 90% to 40% by weight, most preferably from 80% to 50% by weight of a liquid carrier, e.g., water, preferably a mixture of water and organic solvent.

Gel compositions

The detergent compositions of the present invention may also be in the form of gels. Such compositions are typically formulated with polyakenyl polyether having a molecular weight of from about 750,000 to about 4,000,000.

Solid compositions

The detergent compositions of the invention may also be in the form of solids, such as powders and granules.

The mean particle size of the components of granular compositions in accordance with the invention should preferably be such that no more than 5% of particles are greater than 1.4mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The bulk density of granular detergent compositions in accordance with the present invention are particularly useful in concentrated granular detergent compositions that are characterised by a relatively high density in comparison with conventional laundry detergent

compositions. Such high density compositions typically have a bulk density of at least 600 g/litre, more preferably from 650 g/litre to 1200 g/litre, most preferably from 800g/litre to 1000g/litre.

Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

Making processes - granular compositions

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

The invention is illustrated in the following non limiting examples, in which all percentages are on a weight basis unless otherwise stated.

In the bleaching compositions of the invention and detergent compositions incorporating the bleaching compositions of the invention, the abbreviated component identifications have the following meanings:

CXYAS	:	Sodium C ₁₄ -C ₁₅ predominantly linear alkyl sulphate
TAE 50	:	Tallow alcohol ethoxylated with 50 moles of ethylene oxide per mole of alcohol
C ₂₅ E ₃ S	:	Sodium C ₁₂ -C ₁₅ branched alkyl sulphate condensed with three moles of ethylene oxide
C24 E5	:	A C ₁₂ -14 branched primary alcohol condensed with an average of 5 moles of ethylene oxide
NaSKS-6	:	Crystalline layered silicate of formula $\delta\text{-Na}_2\text{Si}_2\text{O}_5$
Carbonate	:	Anhydrous sodium carbonate with a particle size between 200 μm and 900 μm
Zeolite A	:	Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
Percarbonate	:	Sodium Percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
TAED	:	Tetraacetyl ethylene diamine (86% active) agglomerated with MA/AA
Hydrophobic peroxyacid precursor	:	(6-nonanamidocaproyl) oxybenzene sulfonate (72% active) agglomerated with citric acid and TAE 50
Brightener	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino) stilbene-2:2'-disulphonate.
HEDP	:	Hydroxy-ethane 1,1 diphosphonate

DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
Silicone antifoam:		Polydimethylsiloxane foam controller with Siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said
Photoactivated:		dispersing agent of 10:1 to 100:1.
encapsulated in bleach		Sulphonated Zinc Phthalocyanine dextrin soluble polymer
Savinase	:	proteolytic enzyme of standard activity 10T/g
Cellulase	:	cellulytic enzyme of activity 1000 CEVU/g
Termamyl	:	Amylolytic enzyme of activity 60KNU/g
Lipolase	:	Lipolytic enzyme of activity 100kLU/g
Endolase	:	Endoglucanase A of activity 2T/g
		all sold by NOVO Industries A/S
PVNO	:	Polyvinylpyridine N-oxide
PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole
CMC	:	Sodium carboxymethyl cellulose
SRA	:	Sulfobenzoyl end capped esters with oxyethylene
(Soil Release Agents)	:	oxy and terephthaloyl backbone

Example 1

The following perfume formulation was prepared:

Aroma chemicals	%
Hexyl Salicylate	20
Tetrahydromuguol	10
Tetrahydrogeraniol	6
Phenyl ethyl alcohol	8

Cyclopentadecanolide	10
4-tertiary butyl cyclohexyl acetate	10
7-acetyl 1,2,3,4,5,6,7,8 octanhydro 1,1,6,7 tetra methyl naphthalene	9
Hexahydro 4-7-methano-inden-5-yl acetate	5
Methyl phenyl ethyl ketone	4
Acetaldehyde:Phenyl ethyl propyl acetal	7
Iso-amyl phenyl ethyl ether	5
2-tertiary butyl cyclohexyl acetate	4
Phenyl ethyl methyl ether	0.5
Lauric nitrile	0.5
Cis-3-Hexenyl Acetate	0.5
Dynascone 10%	0.5

Example 2

The following detergent compositions according to the invention were prepared, where the perfume is as defined in Example 1.

	Components	A	B
Agglomerate	C25 AS/C45 AS	6.44	6.44
	C25 E3S	1.61	1.61
	Zeolite A	4.61	4.61
	Carbonate	2.10	2.10
	MA/AA	2.51	3.44
	CMC	0.28	0.28
	PVNO/PVPVI	0.02	0.02
	TAED	1.75	-
	Hydrophobic peroxyacid bleach	3.70	4.79
	DTPMP	0.38	0.38
Dry additive	MgSO ₄	0.38	0.38
	Zeolite A	6.90	7.14

	SKS-6/citric	8.50	8.50
	Carbonate	8.25	8.25
	MA/AA	0.65	0.93
	SRA	0.20	0.20
	Savinase	0.60	0.60
	Lipolase	0.14	0.14
	Cellulase	0.19	0.19
	Termamyl	0.40	0.40
	Endolase	0.15	0.15
	Percarbonate	13.25	13.25
	HEDP	0.40	0.40
	Brightener	0.21	0.21
	Photoactivated bleach	0.002	0.002
	Silicone antifoam	2.00	2.00
Spray on	C24 E5	3.10	3.10
	C16-C18 polyhydroxy fatty acid amide	1.33	1.33
	Perfume	0.44	0.44
Minors and miscellaneous to balance			

The compositions in accordance with the invention were all seen having an enhanced perfume stability as well as producing an effective soil removal performance.

What is claimed is:

1. A perfumed bleaching composition containing:
 - a. a hydrophobic bleaching system selected from
 - i) a perhydrate in amount of from 0.1% to 60% by weight and combined with a hydrophobic peroxyacid bleach precursor in amount of from 0.1% to 60% by weight,
 - ii) a preformed hydrophobic peroxyacid in amount of from 0.1% to 60% by weight, and
 - iii) mixtures of i) and ii)
 - b. a perfume composition in amount from 0.05% to 2% by weight which comprises one or more aroma chemicals selected from: tertiary alcohols, nitriles, lactones, ketones, acetals, ethers, schiff bases, esters and mixtures thereof, wherein the total sum of the weight of said aroma chemicals in the perfume is at least 40% by weight of the perfume.
2. A composition according to Claim 1, wherein the backbone chain of the peroxyacid bleach precursor and/or the peroxyacid bleach contains more than 7 carbons.
3. A composition according to Claim 1, wherein said hydrophobic bleach precursor is selected from bleach precursor compounds which comprise at least one acyl group forming the peroxyacid moiety bonded to a leaving group through an -O- or -N- linkage.

4. A composition according to any one of Claim 1-3, wherein said bleach precursor is selected from 3,5,5-tri-methyl hexanoyl oxybenzene sulfonate, nonanoyl oxybenzene sulfonate, an amide substituted peroxyacid precursor compound and any mixtures thereof.
5. A composition according to any one of Claim 1-4, wherein said bleach precursor is an amide substituted peroxyacid precursor compound selected from (6-octanamido-caproyl)oxybenzene sulfonate, (6-nonanamidocaproyl) oxybenzene sulfonate, (6-decanamido-caproyl)oxybenzene sulfonate, and mixtures thereof.
6. A composition according to any one of Claim 1-5, wherein said preformed hydrophobic peroxyacid is an amide substituted peroxyacid compound.
7. A composition according to Claim 6, wherein said preformed hydrophobic peroxyacid bleach is monononylamido peroxycarboxylic acid.
8. A composition according to any one of Claim 1-7, wherein
 - a. said tertiary alcohols are selected from tetrahydro linalool, tetrahydro myrcenol, tetrahydro muguol and tetrahydro geraniol compounds,
 - b. said nitriles are selected from lauric nitrile, myristic nitrile and tridecene-2-nitrile compounds,
 - c. said lactones are selected from undecalactone, hexadecanolide and cyclopentadecanolide compounds,
 - d. said ketones are selected from methyl beta naphtyl ketone, methyl phenyl ethyl ketone and 7-acetyl 1,2,3,4,5,6,7,8 octanhydro 1,1,6,7 tetra methyl naphtalene compounds,

- e. said acetals are selected from (indan-alpha-ole, 2-hydroxymethylene) formald acetal, acetaldehyde: phenyl ethylpropyl acetal and 4-phenyl-2,4,6-trimethyl-1-3-dioxane compounds,
- f. said ethers are selected from iso-amyl phenyl ethyl ether, phenyl ethyl methyl ether, cedryl methyl ether and 3,3,5 trimethyl cyclohexyl ethyl ether compounds,
- g. said schiff bases are selected from lyral/methyl anthranilate, helional/methyl anthranilate and triplal/methyl anthranilate, and
- h. said esters are selected from 2-tertiary butyl cyclohexyl acetate, 4-tertiary butyl cyclohexyl acetate, hexahydro 4-7-methano-inden-5-yl acetate, hexahydro 4-7-methano-inden-6-yl acetate, hexahydro 4-7-methano-inden-5-yl propionate, hexahydro 4-7-methano-inden-6-yl propionate, hexyl salicylate and amylsalicylate compounds.

9. A composition according to any one of Claims 1-8, wherein the total sum of the weight of said aroma chemicals in the perfume is at least 50% by weight of the perfume.
10. A composition according to any one of Claims 1-9, wherein the total sum of the weight of said aroma chemicals in the perfume is at least 60% by weight of the perfume.
11. A detergent composition comprising a surfactant material, a builder and a perfumed bleaching composition as claimed in any one of Claims 1-10.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/02768

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C01B 15/00; C11D 3/395
US CL : 252/95, 186.1, 186.39, 186.42, 186.43

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/95, 186.1, 186.39, 186.42, 186.43, 174.11, 186.26, 186.27, 186.38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,234,617 A (HUNTER et al.) 10 August 1993, see the abstract, examples VII-VIII, and claims 1 and 9.	1-4
X	US 5,248,434 A (NICHOLSON) 28 September 1993, see the abstract, examples VII-VIII, and claim 1.	1-4
X	US 4,923,631 A (SIMS et al.) 08 May 1990, see the abstract, examples I-XIV, and claim 1.	1-4
Y	US 5,106,528 A (FRANCIS et al.) 21 April 1992, see the abstract, and examples 1-3.	1-4

Further documents are listed in the continuation of Box C. See patent family annex.

• Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
• "A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
• "E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
• "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
• "O" document referring to an oral disclosure, use, exhibition or other means		
• "P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

05 JUNE 1996

Date of mailing of the international search report

12 JUL 1996

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US96/02768**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: 5-11 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.